

# Monte Carlo simulation based on dynamic disorder model in organic semiconductors: From bandlike to hopping transport

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The dynamic disorder model for charge carrier transport in organic semiconductors has been extensively studied in recent years. Although it is successful on determining the value of bandlike mobility in the organic crystalline materials, the incoherent hopping, the typical transport characteristic in organic semiconductors, cannot be described. In this work, the decoherence process is taken into account via a phenomenological parameter, say decoherence time, and the projective and Monte Carlo method is applied for this model to determine the waiting time and thus the diffusion coefficient. We find the type of transport changes from bandlike to incoherent hopping with a sufficiently short decoherence time, which indicates the essential role of decoherence time in determining the type of transport in organics. We have also discussed the spatial extent of carriers for different decoherence time, and the transition from delocalization (carrier resides in about 10 molecules) to localization is observed. Based on the experimental results of spatial extent, we estimate the decoherence time in pentacene has the order of 1ps. Furthermore, the dependence of diffusion coefficient on decoherence time is also investigated, and corresponding experiments are discussed.

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## I. INTRODUCTION

It has been long-termly known that, the two different types of charge carrier transport, namely, incoherent hopping and bandlike tunneling, coexist in organic semiconductors, and both of them play an essential role simultaneously.<sup>1,2</sup> At the very beginning, when the conducting conjugated polymer was firstly found in 1970s, the explanation for the underlying mechanism of the electric conductivity was based on the picture of solitons and polarons.<sup>3</sup> It is the strong electron-phonon (e-p) coupling in organic materials that makes the electrons or holes self-trap in a lattice distortion. This charged polaron is the main carrier, which is initially realized to be completely localized in an individual molecule. In this context, it was smoothly concluded that, the character of charge transport between organic molecules should be incoherent hopping of polarons. However, in the last decade, plenty of experiments reported that there is a region that bandlike tunneling works.<sup>2,4-7</sup> For example, there exists an abnormal region around 100-200K that the mobility decreases as temperature increases (i.e., negative temperature coefficient of mobility). This indicates the type of carrier transport in this region is bandlike and coherent,<sup>2</sup> as the charge is found to be delocalized in a region of several molecules (about 10 molecules from the experiment of electron spin resonance<sup>8</sup>) rather than a single molecule. This result is somehow contradiction to the traditional understanding of localized polarons. In addition, it was also stated by a recent experiment on the ultrafast initial carrier dynamics that, the intramolecular microscopic dynamics should be significant in the charge transport.<sup>9</sup> Up to now, to describe the *dualistic* coherent and incoherent transport is still an open subject.

To understand the new experimental findings, a number of theoretical works based on the microscopic mod-

els, such as dynamic disorder model,<sup>10-18</sup> Su-Schrieffer-Heeger (SSH) model,<sup>19</sup> and Anderson model,<sup>20</sup> were addressed to account for the coherent and incoherent transport,<sup>13-15</sup> and the coherent length and diffusion constant<sup>20</sup> have also been studied. Based on Holstein-Peierls model, Troisi and his coworkers highly commended the mechanism of dynamic disorder.<sup>11</sup> They proposed that, due to the scattering with phonons, the carrier will be localized into a small region, and thus the mobility decreases. Their theory may be applied to the temperature dependence of mobility in organic crystal but has not comprehensively described that in organic semiconductors.<sup>21</sup> Meanwhile, under sufficiently long time evolution, the model seems failing to capture the basic bandlike characteristic.<sup>12</sup> More importantly, the Ehrenfest method used by Troisi has some fundamental drawbacks, and the typical one is that the superposition principle is deviated.<sup>22</sup> This is because the decoherence process has not been appropriately taken into consideration,<sup>22</sup> while for the simulation of incoherent hopping transport in organic semiconductors, the decoherence process should be of actual importance.

In the common sense, the role of phonons is twofold: One is to provide the energy to help the carrier hopping (hopping transport) and the other is to scatter with carriers to obstruct them (bandlike transport). These two mechanisms might coexist in organic semiconductors, which makes the discussion on this issue very complicated. In this work, we apply the decoherence process into Troisi's dynamic disorder model<sup>10</sup> and then embed it into the Monte Carlo simulation to quantitatively evaluate the diffusive coefficient within organic molecules. Our aim is to provide a generalized and efficient way to merge the above two roles of phonons into a single framework and find the transition between bandlike and incoherent hopping transport. The paper is organized as follows.

The next section will be the introduction of the present theory. The main results will be in the third section, and the final section is for the conclusions.

## II. INTERPLAY OF INCOHERENT HOPPING AND COHERENT EVOLUTION

In this section, we will introduce the present theory. As the basis, incoherent hopping and thus the decoherence process during intermolecular hopping will be firstly described by introducing a phenomenological parameter, i.e., decoherence time. Then the details of the calculating procedure of diffusion coefficient will be described. At last, the dynamic disorder model will be introduced into the theory.

### A. Incoherent hopping

We first discuss the incoherent hopping, which is the motivation we consider the process of decoherence in this work. Originally, in order to study the incoherent hopping, Bässler applied the kinetic Monte Carlo simulation with the so-called Miller-Abrahams (M-A) formula embedded.<sup>23</sup> Based on the Gaussian disorder model (GDM), he was able to evaluate the relationship between the mobility of carriers and temperature, electric field, and energy disorder. Especially, he found for the temperature dependence of mobility a scaling  $\sim \exp(-T^{-2})$ , which is quite different from the traditional understanding.<sup>23</sup> Following him, there are lots of work investigating the influence of carrier density,<sup>24</sup> electron-electron interactions,<sup>25</sup> and so on.<sup>26</sup> Meanwhile, the other theories, such as the molecular dynamics,<sup>18</sup> the percolation theory,<sup>27,28</sup> and those considering the trapping mechanism,<sup>29,30</sup> are applied extensively to complement the discussions of this incoherent hopping. Especially, the dynamic disorder model has already been put into the Monte Carlo simulation under the displaced harmonic oscillator approximation,<sup>18</sup> which is somehow different from the present treatment.

Fundamentally, the M-A formula, coinciding with the detailed balance, is related to a single phonon process, such that the energy difference between initial and final site must be comparable with the highest energy of phonons that could effectively interact with carriers.<sup>31</sup> Hence, the hopping mechanism based on M-A formula could be described like this:<sup>32</sup> initially a few of vibrational modes (phonons) are excited, such that the carriers could be heated up to make the energy levels of two neighboring sites coincide, and then the phonon transit its energy to the carrier to assist it hopping. This mechanism correspondingly provides an intuitive picture to understand the application of M-A formula in the case of low carrier's density,<sup>33</sup> but in common cases, the vibrational modes are quite diverse, which means the single phonon process loses its efficiency. Hence, a converted

picture of incoherent hopping should be addressed, which is one of the main subject in this work.

### B. Process of decoherence

In organic materials, charge carriers move in a complicated environment, which is mainly composed of the disorders of molecular configurations and vibrations, and decoherence happens incessantly. Normally, the high frequency modes of intermolecular vibration (fast interaction) could be realized to be the source of decoherence, while the lower ones (slow interaction) is referred to a thermal reservoir as in dynamic disorder model discussed in below.<sup>10</sup> The typical decoherence time is of the order 1ps in organic materials with good conductivity,<sup>20</sup> such as in C60, where the frequency of center-of-mass motion is observed to be 1.2THz,<sup>35</sup> but in more amorphous materials, the value should be smaller. The common method treating decoherence in molecular systems is to add some fluctuation and dissipation to the model and evaluate the corresponding Green's function.<sup>36</sup> Obviously, this method is invalid for the dynamic disorder model, in which the motion of lattice sites must be calculated within real spacetime. So here we will describe a more efficient picture for the decoherence process,<sup>34</sup> which is straightforward from a so-called coarse graining method.<sup>22</sup>

To this end, we take two molecules indexed by 1 and 2 as an example, as shown in Fig. 1. Initially, there is a carrier residing in molecule 1 as a localized wavepacket. It will spread following the equation of motion,

$$\frac{\partial}{\partial t}\rho = -\frac{i}{\hbar}[H, \rho], \quad (1)$$

where we have used the tool of density matrix  $\rho \left( \equiv \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \right)$  for convenience to understand decoherence.  $H$  in (1) is the Hamiltonian considering the simplest hopping term of polarons, namely,

$$H = \tau_{12}(C_1^\dagger C_2 + h.c.), \quad (2)$$

where  $C_i^\dagger$  ( $C_i$ ) creates (annihilates) a polaron at  $i$  ( $= 1, 2$ )-th molecule,  $\tau_{12}$  the intermolecular overlap integral of electronic wavefunctions.

When the frequency of vibration is high enough, the vibrational modes make the decoherence happen very quickly,<sup>37,38</sup> such that we can define a decoherence time  $t_d$ , within which the carrier will lose its coherence and the off-diagonal terms  $\rho_{12}$  and  $\rho_{21}$  carrying the phase information of the system vanish.<sup>34</sup> Normally,  $t_d$  is of the order of  $1/\tau_{1,2}$ .<sup>38</sup> After  $t_d$ , the pure density matrix  $\rho$  becomes a statistical mixture, and due to the vanishing of overlap between 1 and 2, the system could be realized to be a classical ensemble with  $\rho_{11}$  and  $\rho_{22}$  the probability that the carrier is residing in molecule 1 and 2, respectively. One can then produce a random number  $r \in [0, 1)$

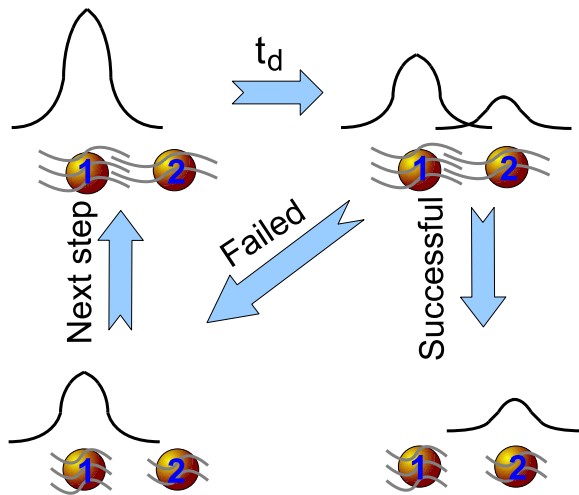


FIG. 1: Schematic for the process of incoherent hopping. Initially, there is a polaron residing in molecule 1. After time  $t_d$ , its wavepacket will spread to molecule 2. Then the correlation between the two molecules is quenched due to the decoherence, and it will be decided whether one try of the incoherent hopping is successful. If yes, the polaron will hop to molecule 2, otherwise the whole process restarts.

as the procedure in Monte Carlo simulation. If  $r < \rho_{22}$ , the carrier will be chosen to reside in molecule 2 after  $t_d$ , and one step of the incoherent hopping finishes. Otherwise, the carrier remains at molecule 1, and the above process restarts. This provides the generalized picture of decoherence.

### C. Evaluation of waiting time

In the common studies of charge transport in organics, the coherent motion of carriers could be simulated within both adiabatic<sup>17</sup> and nonadiabatic<sup>10,19</sup> dynamical method. As well, when one wants to study the incoherent hopping only, the Marcus theory based on lattice relaxation and level crossing is frequently used.<sup>40</sup> Green's function was also evaluated to distinguish incoherent and coherent process.<sup>16</sup> In this subsection, we will develop such a method that merges both coherent and incoherent process on the basis of decoherence as we described above. The central task is that, when a carrier is initially residing in a molecule, we need to find a way to determine the probability that a carrier hops out of the initial molecule.

The procedure of our treatment is as follows. Initially, there is a carrier localized at molecule 1 (or the central site of the chain, as discussed below), that is, the initial state of the system is

$$|I\rangle = |1\rangle \equiv C_1^\dagger |0\rangle. \quad (3)$$

The wavefunction of this carrier will then spread following Eq. (1). Since the carrier loses its coherence every

$t_d$  as discussed above, it will choose a molecule (e.g., molecule 2) to reside in based on the probability at this molecule at  $t_d$ . It means that, we calculate the probability of carrier at molecule 2, i.e.,  $P_2(t_d) (\equiv \langle t_d | C_2^\dagger C_2 | t_d \rangle)$  with  $|t_d\rangle$  the state of system at time  $t_d$ , and then make  $P_2(t_d)$  the hopping probability that the carrier hops out of the initial molecule. This treatment is almost the same with the process of decoherence as we discussed above.

Obviously, when  $t_d$  is small enough, it is extremely difficult for a carrier to hop out of the initial molecule by one try. So the key step of the present theory is that, when the try fails, namely the carrier keeps at the initial molecule, the wavefunction of system will be projected onto the initial molecule, and continue evolving. That is, a new round of evolution starts with the renewed projective initial state

$$|I_{new}\rangle = |1\rangle \langle 1 | t_d \rangle. \quad (4)$$

Again we calculate  $P_2(2t_d)$  after normalizing  $|I_{new}\rangle$  by making the above steps recur. Of course, if necessary,  $t_d$  could also be randomly selected. Now, we have in hand a series of time-dependent  $P_2(kt_d)$ , which is different from those time-independent hopping rates in GDM, so the remaining question is to determine the waiting time  $t_w$  for a carrier residing in the initial molecule. Following the usual idea of Monte Carlo simulation, we sum up  $P_2(kt_d)$  and make the hopping happen when the summation result exceeds a given random number, i.e.,

$$\sum_{k=1}^{k_w} P_2(kt_d) > -\ln \xi, \quad (5)$$

where  $\xi$  is a random number uniformly distributed between 0 and 1. In case for simplicity, the right hand side of (5) could also be replaced by 1. Then the waiting time is

$$t_w = k_w t_d. \quad (6)$$

The above procedure could obviously be generalized for different systems beyond two molecules. In the following, we will apply it to the dynamic disorder model.

Before moving on to the next subsection, we would like to say that, the projective method we describe here is almost the same with the coarse graining method, with the only difference that the projection is acting within the real space other than energy space.<sup>22</sup> So that, the basic drawback of Ehrenfest method we will use shortly, such as the deviation of superposition principle, is overcome in some sense. Meanwhile, the sudden switching method of electronic states in molecular dynamics is used for reference of the Monte Carlo simulation.<sup>39</sup> Equivalently, as we will show later, one can also use a rate equation with the off-diagonal decay term to calculate the diffusion process, which will give similar results with the present theory in some case. But for a multi-site system, since the velocities of decay of the off-diagonal term are not exactly the same, the rate equation becomes quite complicated and inefficient in practise. This is why we consider the projective procedure here.

### D. Dynamic disorder model

The dynamic disorder model recommended by Troisi is a quite simple but efficient one in the study of charge transport in organics.<sup>10,11</sup> The basic idea is to use a one-dimensional SSH-like Hamiltonian to describe the coupling between charge carriers and intermolecular vibrational mode. Since the initial distribution of vibrational mode is dependent on temperature, the disorder introduced by this electron-phonon coupling is changeable with temperature, which implies the original meaning of the words "dynamics disorder". The model Hamiltonian writes,

$$H = H_{\text{ele}} + H_{\text{vib}}. \quad (7)$$

The electronic part is

$$H_{\text{ele}} = - \sum_j [\tau - \alpha(u_{j+1} - u_j)](c_{j+1}^\dagger c_j + h.c.), \quad (8)$$

where  $c_j^\dagger(c_j)$  creates (annihilates) a carrier on the  $j$ -th site.  $u_j$  represents the displacement of the  $j$ -th site.  $\tau$  is the transfer integral and  $\alpha$  is the electron-lattice coupling constant. The vibrational part of Hamiltonian (7) is described as

$$H_{\text{vib}} = \frac{K}{2} \sum_j (u_{j+1} - u_j)^2 + \frac{M}{2} \sum_j \dot{u}_j^2, \quad (9)$$

where  $K$  is the elastic constant between neighbor sites and  $M$  the mass of a site. The parameters are chosen to the similar ones as in [10]. That is,  $K = 14500 \text{amu ps}^{-2}$ ,  $M = 250 \text{amu}$ ,  $\alpha = 100 - 995 \text{cm}^{-1}/\text{\AA}$ ,  $\tau = 30 - 300 \text{cm}^{-1}$ , and the lattice constant is  $4 \text{\AA}$ . The number of site for the chain will be set to sufficiently large, such that the diffusive wavepacket of carrier can not reach the end of the chain.

Based on this Hamiltonian, we could use the Ehrenfest method to calculate the diffusion of an initially localized wavepacket of carrier.<sup>10</sup> The initial state could have several forms and result in slightly different trajectories, but the basic behavior does not change.<sup>41</sup> In this work, the initial electronic state we choose is to locate a carrier at a single site, e.g. the central site of the chain. And the initial condition of vibrations is under thermal equilibrium, i.e.,  $\{u_i\}$  and  $\{\dot{u}_i\}$  will be randomly chosen in a Gaussian distribution with variance  $k_B T/K$  and  $k_B T/M$ , respectively, with  $T$  the temperature. Then we apply the time-dependent Schrödinger equation for electronic part and Newtonian equation for vibrational part to compute the time evolution of the whole system.

In the original treatment of Troisi, the evolution time should be long enough to ensure the saturation of diffusion coefficient. But in the present work, we calculate the evolution for each round to the time  $t_d$  and then make a decision whether the carrier could hop out of the initial site. The whole calculating procedure for electronic

part is almost the same as described in above subsections. However, as we are now facing a multi-site system, we treat the initial site as molecule 1 and the others as molecule 2, and after the hopping is determined, we need to produce another random number to determine which site the electron should go. On the other hand, the evolution of vibrational part will be successive during the decision of the final site of electron. The quantities we compute are the diffusion coefficient defined as

$$D = \langle r^2 \rangle / 2t_w, \quad (10)$$

with  $r$  the distance between the initial site and the final site that the carrier hops to, whose mean value is the diffusion length as we will show in below. Of course, if necessary, the mobility could be calculated by Einstein relation,<sup>10</sup> but Einstein relation is violated under nonequilibrium condition,<sup>43</sup> such that the validity to use it here should be doubted. So we did not plan to plot it in the present work.

## III. RESULTS AND DISCUSSIONS

### A. Comparison with no decoherence case

In Fig. 2, we show the comparison between the present theory and others. Firstly, under the parameters that Troisi has used,<sup>10</sup> we change the value of  $t_d$  and calculate the same quantity with Troisi, i.e., the averaged squared displacement. The red lines are from our projective method, while the blue ones are from the calculation based on the master equation. For the latter case, we add an exponential decay term with variance  $t_d$  for all the off-diagonal elements of the density matrix and calculate the evolution and the physical quantities we want. This treatment is an intuitive way to treat the decoherence at least in two-site systems.

As shown in left panels of Fig. 2, following the  $t_d$  decreasing, the diffusion becomes much slower than Troisi's results, say no decoherence case. Meanwhile, when the  $\tau$  and  $\alpha$  reduce by one order, the reduction of diffusion coefficient becomes quite large. These results clearly show that, when the decoherence is presence, the ability of charge transport becomes poorer, and as we will show shortly, the type transits from bandlike to hopping transport. On the other hand, the results from the present projective method are very close to those from the master equation, but the computational efficiency improves a lot.

### B. Transition from bandlike to hopping transport

The most important characteristic difference between bandlike and hopping transport is that, for the former one the diffusion coefficient decreases with increasing temperature due to the thermal induced dynamic disorder (say, a power law scaling  $\sim T^{-m}$ ), while for the

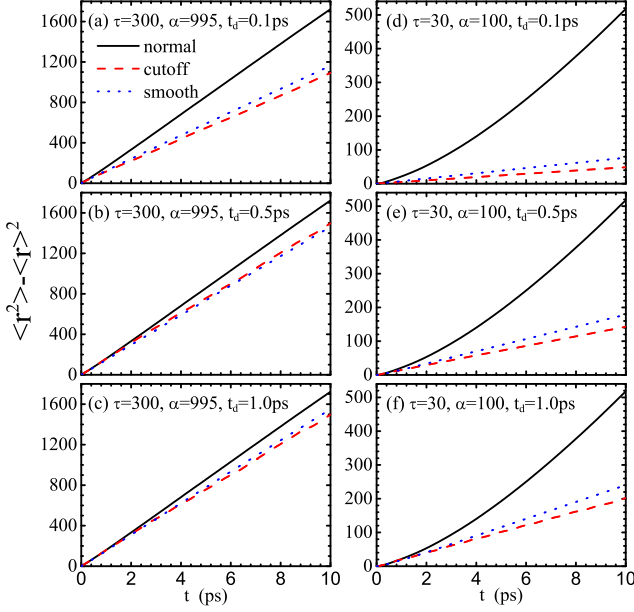


FIG. 2: Averaged squared displacement versus time for different parameters with (red and blue) and without decoherence (black). The red lines are from our projective method, while the blue ones are from the calculation based on the master equation.

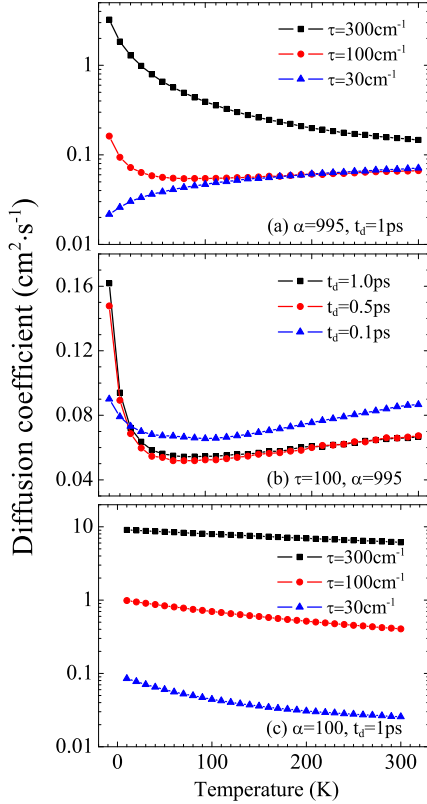


FIG. 3: Diffusion coefficient versus temperature for different  $\tau$ ,  $t_d$ , and  $\alpha$ . The values of  $\alpha$  is in the unit of  $\text{cm}^{-1}/\text{\AA}$ .

latter case the diffusion coefficient increases with increasing temperature due to the thermal assisted mechanism ( $\sim \exp(-T^{-m})$ ). In Troisi's original studies, only bandlike transport was found for all the range of parameters. Here in Fig. 3, we show for different parameters the diffusion coefficient. Our results clearly show that, when  $\tau$  is small ( $\tau = 30\text{cm}^{-1}$ , which is the typical value in organic small molecules), there is only positive temperature dependence of diffusion coefficient. While when  $\tau$  is large ( $\tau = 300\text{cm}^{-1}$ , which is the typical value in pentacene), there is only a negative and power law ( $m \simeq 0.5$ ) temperature dependence. In between ( $\tau = 100\text{cm}^{-1}$ ), both positive and negative temperature dependence emerge. On the other hand, as shown in Fig. 3(b), when we change  $t_d$ , we find a critical region of the transition between bandlike (low temperature) to hopping (high temperature) transport, and the transition point is around 100K. This is the most important finding in this work. The explanation of these results is that, for large  $\tau$ , the case is the same with that discussed in dynamic disorder model,<sup>10</sup> while for small  $\tau$ , the carrier has little time to diffuse to other sites, but some phonon induced potential well could assist carrier to move. So in the latter case, temperature plays a positive role, and the type of transport becomes incoherent hopping. More interpretation will be addressed shortly when we study the diffusion length. In addition, to get the sense of the influence of electron-phonon coupling, we also show the results with  $\alpha = 100\text{cm}^{-1}/\text{\AA}$  in Fig. 3(c). Based upon our calculation, the transition region from bandlike to incoherent hopping is insensitive to  $\alpha$  except some quantitative change, which means the dynamic disorder itself does not influence the transition of the two type of transport.

As we have mentioned, the temperature dependence is mostly negative in crystalline organic semiconductors, whose mechanism should be bandlike transport. Here, applying the physics of decoherence, we obtain both positive and negative temperature dependence for different  $\tau$  and temperature. For the typical value of  $\tau$  in pentacene, namely  $\tau = 300\text{cm}^{-1}$ , it shows negative temperature dependence, which is the same with the result in dynamic disorder model.<sup>10</sup> It implies that, in this material, bandlike mechanism dominates the charge transport, and the role of decoherence is just to decrease the diffusion coefficient as we will discuss later on. However, the value of  $\tau$  in other organic materials, such as  $\text{Alq}_3$ , is about two order smaller than that in pentacene, i.e.,  $< 30\text{cm}^{-1}$ , so the temperature dependence becomes positive. Hence, in common organic semiconductors under room temperature, the characteristic of hopping transport should be more frequently observed.

### C. Spatial extent of carriers

The spatial extent of carriers is a controversial but crucial issue in this field. Understanding of it is essentially helpful to clarify the interplay between bandlike and hop-

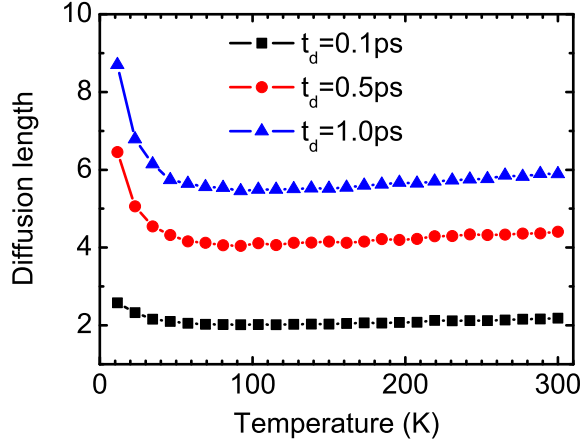


FIG. 4: Diffusion length (in the unit of the number of site) versus temperature for different  $t_d$ .  $\tau = 100\text{cm}^{-1}$  and  $\alpha = 995\text{cm}^{-1}/\text{\AA}$

ping transport. The former corresponds to a delocalized picture, while the latter is to the localized one. Especially, since the localization length in pentacene is estimated to be about 10 molecules,<sup>8</sup> this value could be directly utilized to estimate the decoherence time in pentacene. Within the present theory, we can also calculate the diffusion length within  $t_w$  as the average distance between initial and final site that before and after carrier hops. Obviously, when  $t_d$  is very large, our result should be the same with Troisi's.<sup>10</sup> In Fig. 4, it is found that, with  $t_d \simeq 0.5 - 1\text{ps}$ , the carrier could diffuse over about 5 sites, that is, the spatial extent of the carrier is about 10 times intermolecular distance, which is very close to the experimental prediction in pentacene.<sup>8</sup> Hence, we can safely say that, 1ps is the typical order of decoherence time in pentacene. Besides, with small  $t_d$ , the carrier is only localized within the next-nearest sites, such that, hopping transport should be the dominant for this case. Correspondingly, with temperature increasing, the large  $t_d$  curves decrease first and then increase slightly, while the small  $t_d$  curve does almost not change. This means, for the bandlike transport, the spatial extent of carriers should decrease with increasing temperature, while for the hopping transport, the carrier is mainly localized. The results for other parameters are similar, so we do not show here.

The physical picture of these results is quite different from that in the traditional understanding of incoherent hopping, where the carrier residing in a trap would tunnel to another one with similar energy.<sup>32</sup> This mechanism works based upon the simple phonon structure and dilute impurities in inorganic semiconductors. In organic semiconductors, however, due to the dynamic disorder each molecule might be treated as a trap and the phononic environment is quite diverse. So the basic point for the dynamics disorder model is, in our opinion, not the energy difference between molecules, but how long the carrier spreads. Fig. 5 shows a brief schematic for the present

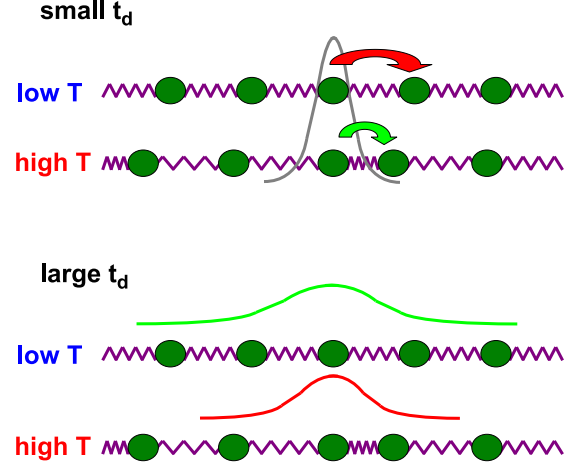


FIG. 5: Schematic for the transition between hopping and bandlike transport. Under low temperature, the configuration of molecules is regular, while under high temperature, it is disordered. For small  $t_d$ , the carrier is mainly localized in one molecule, such that temperature acts as an assistance. For large  $t_d$ , the wavepacket of carrier is extended, and temperature produces disorders for the carrier's diffusion.

theory. When  $t_d$  is small, the hopping is mainly between two neighbor molecules. In this case, due to the thermal motion of each molecule, the intermolecular distance eventually decreases when the temperature is sufficiently high, such that the hopping rate should be larger than that under low temperature. This is actually the temperature assisted hopping. While when  $t_d$  is large, that is, the carrier is much easier to spread out to several sites, the thermal motion of molecules behaves now as the disordered obstacles. So in this case, temperature will act to produce more and more scattering to the carriers and then block the carrier's motion.

#### D. Diffusion coefficient versus $t_d$

In the present theory, the decoherence time  $t_d$  is the most important parameter. In Fig. 6, we show the dependence of diffusion coefficient on  $t_d$ . As expected, the diffusion coefficient increases following the increasing  $t_d$ , and when  $t_d > 2\text{ps}$ , diffusion coefficient tends to saturate to the result from Troisi.<sup>10</sup> This is easy to understand, since when  $t_d$  is extremely small, it is quite hard for a carrier to hop out of the initial site. It is worth noting that, the estimated value of mobility in dynamics disorder model is slightly larger than that from experiment, say  $3\text{cm}^2\text{s}^{-1}\text{V}^{-1}$  from theory and  $1\text{cm}^2\text{s}^{-1}\text{V}^{-1}$  from experiment.<sup>10</sup> The present theory based on the decoherence might be the solution to this difference. Furthermore, the experiment on organic field effect transistor has shown that, when the drain voltage is large, the temperature coefficient is negative, and for the inverse case, it is positive.<sup>2</sup> This could also be explained in the present theoretical framework. In case the drain volt-

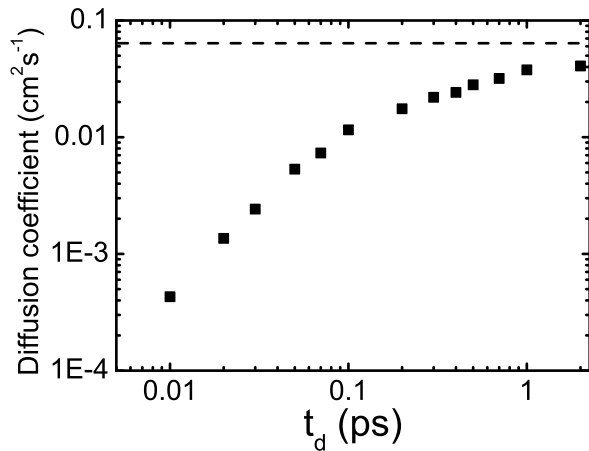


FIG. 6: Diffusion coefficient versus  $t_d$ .  $\tau = 300\text{cm}^{-1}$ ,  $\alpha = 995\text{cm}^{-1}/\text{\AA}$ , and  $T = 300\text{K}$ . The dashed line denotes the diffusion coefficient obtained in Ref. [10].

age is large, the waiting time  $t_w$  in each molecule should be small. Considering the ratio between  $t_w$  and  $t_d$  that, the smaller the  $t_w$ , the larger the  $t_d$ , the relationship of mobility with drain voltage could be easily understood.

#### IV. CONCLUDING REMARKS

Actually, the influence of phonons on charge transport in organic semiconductors has been studied extensively in the literature. However, the meaning of "incoherent hopping" in organic materials is still obscure in our opinion, since the widely used M-A formula is not such applicable for organic molecules. Meanwhile, as we show in this work, hopping and bandlike transport happens at different time scales. The first case refers to decoherence time of the same order with relaxation time of phonon so that phonon is able to transfer its energy to the carrier to assist it hopping, while the second case functions when  $t_d$

is large enough to ensure the time for scattering between carriers and phonons. In a real material, there are many ways to adapt these two conditions and make the type of transport transit from hopping to bandlike. Furthermore, under low temperature, tunneling might become dominating, and carriers will search for a molecule out of the trap which has closest energy to tunnel to, i.e., Mott's variable range hopping mechanism.<sup>32</sup> This case has not been addressed in the present work.

In the end, we would like to discuss more on the present theory. Firstly, the practical device parameters, such as electric field, have not been explicitly included, which could be easily considered within the present framework. For example, the electric field could be regarded as a phase factor in the hopping constant,<sup>42</sup> but for the common Ehrenfest method, this way loses its efficiency due to the Bloch oscillation. Especially, based on the study of electric field, we might discuss the validity of Einstein relation in these systems.<sup>43</sup> Secondly, it is straightforward to replace the dynamic disorder model discussed in the present work, such as Holstein model, spin-boson model, etc. Especially, since the spin motion in organic materials is always realized to be coherent, it could be easily incorporated into the present theory, and the hot debated magnetic field effect could be studied.<sup>44</sup> Thirdly, the theory could be applied to estimate the corresponding decoherence time in the specific material, since it is the only adjustable parameter.

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<sup>1</sup> For a review, see V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey, and J. Bredas, *Chem. Rev.* **107**, 926 (2007).

<sup>2</sup> T. Sakanoue and H. Sirringhaus, *Nature Mater.* **9**, 736 (2010); J. F. Chang, T. Sakanoue, Y. Olivier, T. Uemura, M. Dufourg-Madec, S. G. Yeates, J. Cornil, J. Takeya, A. Troisi, and H. Sirringhaus, *Phys. Rev. Lett.* **107**, 066601 (2011).

<sup>3</sup> W. P. Su, J. Schrieffer, and A. Heeger, *Phys. Rev. Lett.* **42**, 1698 (1979).

<sup>4</sup> A. Salleo, T. W. Chen, A. R. Völkel, Y. Wu, P. Liu, B. S. Ong, and R. A. Street, *Phys. Rev. B* **70**, 115311 (2004).

<sup>5</sup> V. Podzorov, E. Menard, A. Borissov, V. Kiryukhin, J. A. Rogers, and M. E. Gershenson, *Phys. Rev. Lett.* **93**, 086602 (2004).

<sup>6</sup> N. Karl, *Synthetic Metals* **133**, 649 (2003).

<sup>7</sup> M. Kemerink, T. Hallam, M. J. Lee, N. Zhao, M. Caironi, and H. Sirringhaus, *Phys. Rev. B* **80**, 115325 (2009).

<sup>8</sup> K. Marumoto, S. Kuroda, T. Takenobu, and Y. Iwasa, *Phys. Rev. Lett.* **97**, 256603 (2006).

<sup>9</sup> A. Devizis, K. Meerholz, D. Hertel, and V. Gulbinas, *Phys. Rev. B* **82**, 155204 (2010).

<sup>10</sup> A. Troisi and G. Orlandi, *Phys. Rev. Lett.* **96**, 086601 (2006).

<sup>11</sup> A. Troisi and D. L. Cheung, *J. Chem. Phys.* **131**, 014703 (2009).

<sup>12</sup> S. Ciuchi, S. Fratini, and D. Mayou, *Phys. Rev. B* **83**, 081202(R) (2011).

<sup>13</sup> S. Fratini and S. Ciuchi, *Phys. Rev. Lett.* **103**, 266601 (2009).

<sup>14</sup> Y. -C. Cheng and R. J. Silbey, *J. Chem. Phys.* **128**, 114713 (2008).

- <sup>15</sup> F. Ortmann, F. Bechstedt, and K. Hannewald, Phys. Rev. B **79**, 235206 (2009).
- <sup>16</sup> K. Hannewald, V. M. Stojanović, J. M. T. Schellekens, P. A. Bobbert, G. Kresse, and J. Hafner, Phys. Rev. B **69**, 075211 (2004).
- <sup>17</sup> S. Ciuchi and S. Fratini, Phys. Rev. B **79**, 035113 (2009).
- <sup>18</sup> L. Wang, Q. Li Z. Shuai, L. Chen and Q. Shi, Phys. Chem. Chem. Phys. **12**, 3309 (2010).
- <sup>19</sup> Z. An, C. Q. Wu, and X. Sun, Phys. Rev. Lett. **93**, 216407 (2004).
- <sup>20</sup> J.-D. Picon, M. N. Bussac, and L. Zuppiroli, Phys. Rev. B **75**, 235106 (2007).
- <sup>21</sup> D. P. McMahon and A. Troisi, ChemPhysChem **11**, 2067 (2010).
- <sup>22</sup> E. R. Bittner and P. J. Rossky, J. Chem. Phys. **103**, 8130 (1995).
- <sup>23</sup> H. Bässler, Phys. Stat. Sol. (b) **175**, 15 (1993).
- <sup>24</sup> J. Zhou, Y. C. Zhou, J. M. Zhao, C. Q. Wu, X. M. Ding, and X. Y. Hou, Phys. Rev. B **75**, 153201 (2007); W. F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P. A. Bobbert, P. W. M. Blom, D. M. de Leeuw, and M. A. J. Michels, Phys. Rev. Lett. **94**, 206601 (2005); R. Coehoorn, W. F. Pasveer, P. A. Bobbert, and M. A. J. Michels, Phys. Rev. B **72**, 155206 (2005).
- <sup>25</sup> J. Zhou, Y. C. Zhou, X. D. Gao, C. Q. Wu, X. M. Ding, and X. Y. Hou, J. Phys. D: Appl. Phys. **42**, 035103 (2009).
- <sup>26</sup> C. Deibel, T. Strobel, and V. Dyakonov, Phys. Rev. Lett. **103**, 036402 (2009); T. Strobel, C. Deibel, and V. Dyakonov, Phys. Rev. Lett. **105**, 266602 (2010).
- <sup>27</sup> A. L. Efros and B. I. Shklovskii, *Electronic Properties of Doped Semiconductors* (Springer-Verlag, Berlin, 1984).
- <sup>28</sup> M. C. J. M. Vissenberg and M. Matters, Phys. Rev. B **57**, 12964 (1998).
- <sup>29</sup> J. Nelson, Phys. Rev. B **67**, 155209 (2003).
- <sup>30</sup> M. Koehler and I. Biaggio, Phys. Rev. B **68**, 075205 (2003); R. Coehoorn, W. F. Pasveer, P. A. Bobbert, and M. A. J. Michels, Phys. Rev. B **72**, 155206 (2005); S. J. Konezny, M. N. Bussac, and L. Zuppiroli, Appl. Phys. Lett. **95**, 263311 (2009); S. J. Konezny, M. N. Bussac, and L. Zuppiroli, Phys. Rev. B **81**, 045313 (2010).
- <sup>31</sup> D. Emin, Phys. Rev. Lett. **32**, 303 (1974).
- <sup>32</sup> V. Ambegaokar, B. I. Halperin, and J. S. Langer, Phys. Rev. B **4**, 2612 (1971).
- <sup>33</sup> N. I. Craciun, J. Wildeman, and P. W. M. Blom, Phys. Rev. Lett. **100**, 056601 (2008).
- <sup>34</sup> M. Schlosshauer, *Decoherence and the quantum-to-classical transition* (Springer-Verlag, Berlin Heidelberg, 2010).
- <sup>35</sup> H. Park, J. Park, A. K. L. Lim, E. H. Anderson, A. P. Alivisatos, and P. L. McEuen, Nature **407**, 57 (2000).
- <sup>36</sup> H. M. Pastawskia, L.E.F. Torres, and E. Medina, Chem. Phys. **281**, 257 (2002).
- <sup>37</sup> A. Lucke, C. H. Mak, R. Egger, J. Ankerhold, J. Stockburger, and H. Grabert, J. Chem. Phys. **107**, 8397(1997).
- <sup>38</sup> S. Paganelli and S. Ciuchi, J. Phys: Condens. Matter **20**, 235203 (2008).
- <sup>39</sup> J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).
- <sup>40</sup> L. Wang, Q. Li, Z. Shuai, L. Chen, and Q. Shi, Phys. Chem. Chem. Phys., **12**, 3309 (2010).
- <sup>41</sup> L. Wang, D. Beljonne, L. Chen, and Q. Shi, J. Chem. Phys. **134**, 244116 (2011).
- <sup>42</sup> J. F. Yu, C. Q. Wu, X. Sun, and K. Nasu, Phys. Rev. B **70**, 064303 (2004).
- <sup>43</sup> G.A. H. Wetzelaer, L. J. A. Koster, and P. W. M. Blom, Phys. Rev. Lett. **107**, 066605 (2011).
- <sup>44</sup> Y. Yao, W. Si, and C. Q. Wu, Synthetic Metals **161**, 632 (2011).